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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(54) Title: POLYMER SUPPORTED CATALYST FOR OLEFIN POLYMERIZATION (57) Abstract <p>The present invention is directed to a supported metallocene catalyst useful in the polymerization of <math>\alpha</math>-olefins which is obtained by tethering a metallocene catalyst component to the surface of a particulate functionalized copolymeric support material.</p>		

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1 POLYMER SUPPORTED CATALYST FOR OLEFIN POLYMERIZATION

The present invention relates to a supported  
metallocene catalyst useful for polymerizing or  
copolymerizing  $\alpha$ -olefins. More particularly, the  
5 instant invention is directed to a supported  
metallocene catalyst which is prepared by tethering a  
metallocene catalyst component to a functionalized  
copolymeric support material. The instant invention  
10 also relates to a process for polymerizing or  
copolymerizing  $\alpha$ -olefins using the supported  
metallocene catalysts of the present invention.

Traditionally, ethylene and 1-olefins have  
been polymerized or copolymerized in the presence of  
hydrocarbon insoluble catalyst systems which comprise  
15 a transition metal component and an aluminum alkyl.  
More recently, active homogeneous catalyst systems  
comprising a bis(cyclopentadienyl)-transition metal  
dialkyl, an aluminum alkyl, and water have been found  
to be useful for the polymerization of ethylene. Such  
20 catalyst systems containing a cyclopentadienyl moiety  
are referred to in the art as "metallocenes".

U. S. Patent Nos. 4,404,344; 4,522,982;  
4,590,914 and 4,937,299 describe various homogeneous  
metallocene catalyst systems for use in  $\alpha$ -olefin  
25 polymerization reactions. These metallocene catalyst  
systems typically require the use of an aluminoxane  
compound as a catalyst activator.

An advantage of the metallocene aluminoxane  
homogeneous catalyst system is the very high activity  
30 obtained for ethylene polymerization. Another  
significant advantage is, unlike olefin polymers

1 produced in the presence of conventional heterogeneous  
Ziegler catalysts, terminal unsaturation is present in  
polymers produced in the presence of these homogeneous  
catalysts. Nevertheless, the homogeneous metallocene  
5 catalysts suffer from a disadvantage, that is, the  
ratio of alumoxane to metallocene is high, for  
example, in the order of 1,000 to 1 or greater. Such  
voluminous amounts of alumoxane would require  
extensive treatment of polymer product obtained in  
10 order to remove the undesirable aluminum. A second  
disadvantage of the homogeneous catalyst system, a  
disadvantage also associated with traditional  
heterogeneous Ziegler catalysts, is the multiple  
delivery systems required for introducing the  
15 individual catalyst components into the polymerization  
reactor.

In an attempt to overcome these problems  
mentioned hereinabove, supported-heterogeneous  
metallocene catalyst systems have been developed.  
20 Typically, the heterogeneous metallocene catalyst  
system comprises supporting a metallocene catalyst  
component on refractory inorganic oxide supports, such  
as  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{MgO}$ . These inorganic oxide  
supports, which may be used in concert with an  
25 organoaluminum compound, are available in a variety of  
particle sizes and porosities. One such heterogeneous  
catalyst system using a refractory oxide support is  
described in U.S. Patent No. 5,086,025 to Chang. More  
specifically, the Chang reference discloses a process  
30 for preparing a supported metallocene alumoxane  
catalyst for use in liquid or slurry phase

1 polymerization of  $\alpha$ -olefins. The preparation of the  
supported heterogeneous catalyst involves initially  
reacting silica gel with an aluminum trialkyl solution  
to form a support material for the metallocene  
5 component. The metallocene component is then adsorbed  
onto the surface of the support material.

Despite their usefulness, inorganic oxide  
supports have several deficiencies. For example,  
inorganic oxide supports must be calcined at high  
10 temperatures or chemically treated with appropriate  
reagents to remove physically adsorbed water from the  
surface of the support. The presence of water on the  
surface of inorganic oxide supports is well known in  
the art as being a catalytic poison which can  
15 adversely affect the catalytic activity of the  
catalyst.

In addition, inorganic oxide supports have a  
limited maximum pore size which also can restrict the  
catalytic performance of the catalyst. Although large  
20 pore size inorganic oxides are available, these  
materials may be friable and the use thereof as  
catalyst supports may, through attrition, lead to the  
formation of unwanted fine particles.

Furthermore, it is well known in the art  
25 that inorganic oxides not only adsorb water but other  
commonly occurring catalyst poisons, such as oxygen.  
Thus, great care in handling and preparing inorganic  
oxide supported catalysts must always be exercised.

Moreover, since prior art supported  
30 metallocene catalysts involve adsorption of the  
metallocene onto the inorganic oxide support, a debate

1 exists as to whether the metallocene component is  
actually bound to the surface of the inorganic oxide  
support or is held in place as a contact ion pair in  
conjunction with the surface bound organometallic  
5 species. If the former is the case, the bound complex  
may have been the result of chloride or ligand  
abstraction, or the surface oxygen from the support  
may have been bound to the transition metal. If the  
latter is true, the possibility of active site  
10 migration, redistribution, and bimolecular  
deactivation becomes more reasonable during  
polymerization. All of these phenomena may contribute  
towards poor morphological control or less than  
optimal catalyst performance.

15 To overcome the above deficiencies that are  
commonly observed in inorganic supported catalysts and  
to provide a metallocene catalyst which maintains its  
basic ligand environment and oxidation state, many  
research groups have focused on substituting polymeric  
20 supports for inorganic oxide supports. See, for  
example, U. S. Patent Nos. 4,147,644; 5,206,199; and  
5,346,925; European Patent Appln. Nos. 598,543;  
285,443 and 295,312; and Canadian Patent Appln. No.  
2,093,056.

25 Another example of supporting a metallocene  
catalyst component on a polymeric support is disclosed  
in Japanese Kokai Patent Appln. No. Hei 6-56928  
(1994). The supported metallocene catalyst disclosed  
in this Japanese reference is prepared by reacting a  
30 ligand



1 leader of a transition metal component having halogen  
atoms or an OR group, wherein R is a C<sub>1</sub>-C<sub>16</sub>  
hydrocarbon, with an organometallic compound  
containing a metal from Groups I-III of the Periodic  
5 Table of Elements. Next, the polymeric support  
material having a substitute group, such as a halogen  
atom, an ester group, a carboxyl group or a hydroxy  
group, is reacted and the ligand is chemically bonded  
to the polymeric support. The transition-metal  
10 compound precursor obtained above is then coordinated  
to the ligand chemically bonded to the polymeric  
support material.

Typically, polymeric supports employed in  
the prior art are organic polymers such as  
15 polyethylene, polypropylene, polystyrene, polyvinyl  
alcohol, poly(styrene-divinylbenzene),  
poly(methylmethacrylate) and the like.

The use of these polymeric supports provides  
several advantages over similar olefin metallocene  
20 polymerization catalyst components supported upon  
inorganic oxides. For example, polymeric supports  
usually require no dehydration prior to the use  
thereof; they can be easily functionalized which  
afford more opportunities to prepare tailor-made  
25 catalysts; they are inert; they can be prepared with a  
wide range of physical properties, via chemical and  
mechanical means to intentionally give porosity,  
morphology and size control to the catalyst; and they  
offer a cost advantage over inorganic oxide supports.

30 Despite the advantages listed hereinabove,  
prior art polymeric supports still possess certain

1 inherent disadvantages which decrease their  
acceptability as viable replacements for inorganic  
oxide supports. For instance, polymeric supports  
often lack structural stability at high temperatures  
5 and under some solvent conditions. Moreover, the  
porosity and size of the polymeric support, due to  
swelling may change drastically over the short time  
duration required to prepare the catalyst.  
Furthermore, the choice of the polymer support must be  
10 compatible with the polymer produced in order to  
insure that this incompatibility does not contribute  
to the formation of gels.

It would thus be highly advantageous to  
provide a polymeric support which keeps the active  
15 site of the metallocene intact and which overcomes the  
above drawbacks while still being useful in the  
polymerization of  $\alpha$ -olefins.

The present invention is directed to a  
supported metallocene catalyst that is useful in the  
20 homopolymerization or copolymerization of  $\alpha$ -olefins  
which is prepared by tethering a metallocene catalyst  
component to a particulate functionalized copolymeric  
support material. More particularly, the supported  
metallocene catalyst of the instant invention is  
25 prepared by tethering a metallocene to a particulate  
functionalized copolymeric support through a bridge to  
the cyclopentadienyl, indenyl or fluorenyl ring. The  
particulate functionalized copolymeric supports of the  
instant invention include copolymers of an  $\alpha$ -olefin  
30 and an acrylate, the latter being used in a generic  
sense to include esters of acrylic as well as

1 methacrylic acid. The supported metallocene catalyst  
of the instant invention, in combination with suitable  
cocatalysts, provides an  $\alpha$ -olefin polymerization  
catalyst system which produces polymers comprised  
5 predominantly of ethylene and/or propylene with  
densities ranging from about 0.90 to about 0.97 and  
having a desirable balance of rheological and physical  
properties making them useful in a wide range of  
applications.

10 Specifically, the present invention relates  
to a supported metallocene catalyst useful for  
polymerizing olefins comprising the product which is  
prepared by the steps of (a) reacting a particulate  
olefin copolymer support which comprises discrete  
15 particles having a median particle size ranging from  
about 1 up to about 1500 microns, a pore volume of  
less than 0.1 cc/g and a surface area of less than  
about 15 m<sup>2</sup>/g, wherein said olefin copolymer has a  
melt index of from about 0.1 to about 400 and  
20 containing from about 50.1 to about 99.9 weight  
percent C<sub>2-1</sub>  $\alpha$ -olefin and from about 0.1 to about 49.9  
weight percent of an acrylate, with a metallated  
compound containing a metal from Groups I-III of the  
Periodic Table of Elements under conditions sufficient  
25 to form a metallated keto-intermediate; (b) contacting  
said metallated keto-intermediate of step (a) with a  
transition metal compound having the formula



wherein Cp is a substituted or unsubstituted  
30 cyclopentadienyl, indenyl or fluorenyl ring; M is a  
metal from Group IVB, VB and VIB of the Periodic Table

1 of Elements; R" is a hydride, a hydrocarbyl group  
having from about 1 to about 20 carbon atoms, an  
alkoxy group having from about 1 to about 12 carbon  
atoms, a substituted or unsubstituted aryl group  
5 containing from about 6 to about 12 carbon atoms, or  
NR"', wherein R"' is an alkyl containing from about 1  
to about 12 carbon atoms; X is a halide; a is 0 or 1;  
b is 0-4; c is 0-4; and the sum of a, b, and c is  
equal to the oxidation state of M; and (c) recovering  
10 said contact product of step (b).

In accordance with a preferred embodiment of  
the present invention, the particulate functionalized  
copolymeric support is a microfine powder comprised of  
particles that are spherical or substantially  
15 spherical. The term "microfine" means that the  
particles of the support material have a median  
particle size of from about 1 to about 500 microns.  
The microfine powders which are employed in the  
present invention are prepared by heating a copolymer  
20 to a temperature above the melting point of the  
copolymer in the presence of a nonionic surfactant;  
dispersing the mixture produced in the heating step in  
a dispersant to produce droplets of a desired size;  
and cooling the dispersion to a temperature below the  
25 melting point of the copolymer.

The present invention is also directed to a  
process for polymerizing one or more  $\alpha$ -olefins. In  
this process at least one  $\alpha$ -olefin is polymerized  
under olefin polymerization conditions utilizing the  
30 catalyst system of the present invention which  
includes the tethered metallocene as the solid

1 catalyst component, along with a suitable cocatalyst  
component(s).

The particulate functionalized copolymeric  
supports of the instant invention are copolymers of an  
5  $\alpha$ -olefin and an acrylate. The term "acrylate" being  
used in the generic sense to encompass esters of both  
acrylic and methacrylic acid.

The copolymers, from which the particulate  
functionalized supports of the present invention are  
10 obtained, are produced by copolymerizing an  $\alpha$ -olefin,  
especially ethylene and/or propylene, with one or more  
monomers selected from the group consisting of lower  
alkyl acrylates, arylacrylates and methacrylate  
monomers or by grafting one or more of the  
15 aforementioned acrylate monomers to a polyolefin,  
particularly a polypropylene or polyethylene,  
backbone.

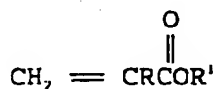
Copolymerizations of  $\alpha$ -olefins and the above  
monomers are well known and are generally carried out  
20 at pressures of up to about 30,000 psi and  
temperatures of from about 150°C to about 250°C in the  
presence of suitable catalysts. A typical process for  
copolymerizing ethylene and lower alkyl acrylates is  
described in U.S. Patent No. 2,200,429, the contents  
25 of which are incorporated herein by reference.

Grafting of the above acrylate monomers onto  
a polyolefin backbone may be conducted by using  
techniques that are well known in the art. Typical  
grafting processes that may be used in the present  
30 invention to graft the acrylate monomer to a  
polyolefin backbone are described in U.S. Patent Nos.

1 2,987,501; 3,027,346 and 3,882,194, the contents of which are incorporated by reference.

The above-mentioned copolymers have an  $\alpha$ -olefin as the major constituent. More preferably, the  
5 copolymers of the invention have from about 50.1 to about 99.9 weight percent  $C_{2-4}$   $\alpha$ -olefin copolymerized with from about 0.1 to about 49.9 weight percent of the monomer. Preferably, the copolymers will contain from about 70 to about 99 weight percent ethylene,  
10 propylene or mixtures thereof and from about 1 to about 30 weight percent of one of the above-identified monomers. In one highly useful embodiment, the copolymer supports comprise from about 80 to about 95 weight percent ethylene and about 5 to about 20 weight  
15 percent acrylate.

The acrylate monomer utilized in the present invention has the formula



20 where R is hydrogen or methyl and R' is an alkyl group having from about 1 to about 12 carbon atoms or an aryl group having from about 6 to about 12 carbon atoms. Alkyl groups may be straight chain or branched  
25 and can be saturated or unsaturated. Aryl groups can be unsubstituted, e.g., phenyl, or can contain one or more hydrocarbyl substituents, e.g., benzyl, tolyl, xylyl.

Representative acrylate comonomers which can  
30 be used for the copolymer include: methyl acrylate, ethyl acrylate, isopropyl acrylate, allyl acrylate, n-

- 1 butyl acrylate, t-butyl acrylate, neopentyl acrylate,  
n-hexyl acrylate, cyclohexyl acrylate, benzyl  
acrylate, phenyl acrylate, tolyl acrylate, xylyl  
acrylate, 2-ethylhexyl acrylate, 2-phenylethyl  
5 acrylate, n-decyl acrylate, isobornyl acrylate, n-  
octadecyl acrylate, methyl methacrylate, ethyl  
methacrylate, propyl methacrylate, n-butyl  
methacrylate, sec-butyl methacrylate, n-pentyl  
methacrylate, n-hexyl methacrylate, n-octyl  
10 methacrylate, isooctyl methacrylate, isodecyl  
methacrylate, lauryl methacrylate and the like.

Among the preferred acrylate comonomers,  
alkyl acrylate comonomers having the above structural  
formula where R is hydrogen and R' is a C<sub>1</sub>, alkyl group  
15 are particularly useful. Of these, methyl acrylate,  
ethyl acrylate and n-butyl acrylate are especially  
preferred. In a highly useful embodiment of the  
invention, the particulate supports are ethylene-  
methyl acrylate, ethylene-ethyl acrylate and ethylene-  
20 n-butyl acrylate copolymers. An ethylene-methyl  
acrylate particulate support is particularly  
preferred.

The melt index of the copolymers can range  
from about 0.1 up to about 400 g/10 min. or above.  
25 However, in a preferred embodiment where the supports  
are microfine powders comprised of particles which are  
spheroidal or substantially spheroidal, the melt index  
is in the range of from about 1 up to about 125, and  
more preferably, from about 1 up to about 60. All  
30 melt indexes referred to herein are determined at

1 190°C in accordance with ASTM D 1238, Condition E, and  
are expressed in grams per 10 minutes.

The copolymers used to form the supported  
metallocene catalysts of the invention are particulate  
5 products comprised of discrete particles whose median  
particle size can range from about 1 up to about 1500  
microns, and more preferably, from about 1 to about  
1000 microns. Moreover, the particulate support  
material of the present invention is further  
10 characterized as having a pore volume of less than  
about 0.1 cc/g and a surface area which is less than  
about 15m<sup>2</sup>/g.

The copolymer powders can be obtained by  
spray drying or the copolymer can be precipitated from  
15 solution by the addition of a suitable precipitating  
agent, e.g., methanol. The particulate supports  
obtained by spray drying the copolymer or copolymers  
may also be ground or milled to produce powders within  
the acceptable size range. Mechanical grinding may be  
20 carried out under ambient conditions if the copolymer  
has a sufficiently high melting point and does not  
degrade under the grinding conditions; however, it is  
more customary to cryogenically grind the copolymers.  
After grinding, the powders can be sieved to recover  
25 particles of the desired size and particle size  
distribution. Suitable particulate supports can also  
be produced using other conventional solution and  
dispersion processes.

In a particularly useful embodiment of the  
30 invention, the supports are "microfine" powders of  
functionalized copolymers obtained by dispersion



1 processes. Particles produced by these processes are  
spheroidal or substantially spheroidal in shape.  
Microfine powders produced using dispersion processes,  
in addition to being spheroidally shaped particles,  
5 also have substantially narrower particle size  
distributions than reactor powders or powders produced  
by precipitation, grinding or milling.

Preferred microfine functionalized  
copolymeric supports are comprised of discrete  
10 particles which are spheroidally or substantially  
spheroidally shaped and have a median particle size  
(diameter) of from about 1 micron to about 500  
microns. More preferably, the median particle size is  
from about 5 microns to about 300 microns and in an  
15 especially useful embodiment the median particle size  
is from about 20 to about 200 microns. Median  
diameters as used herein are obtained from the  
particle volume distribution curve.

The copolymers of the present invention are  
20 converted to microfine powders using the dispersion  
technique of U.S. Patent Nos. 3,422,049, 3,432,483 and  
3,745,681, details of which are incorporated herein by  
reference. In the powder-forming operation, the  
copolymer is charged to the reactor with a polar  
25 liquid medium and nonionic surfactant and a dispersion  
is formed in accordance with conventional dispersing  
procedures described in the art. The dispersing  
apparatus may be any device capable of delivering  
sufficient shearing action to the mixture at elevated  
30 temperature and pressure. Conventional propeller  
stirrers designed to impart high shear can be used for

1 this purpose. The vessel may also be equipped with  
baffles to assist in dispersing the copolymer.  
Particle size and particle size distribution will vary  
depending on the shearing action which, in turn, is  
5 related to the stirrer design and rate of stirring.  
Agitation rates can vary over wide limits but the  
speed of the stirrer will usually be controlled so  
that the tip speed is between about 400 and about 4000  
ft/min and, more commonly, about 800 and about 3500  
10 ft/min. Higher tip speeds are generally used for  
batch operation, usually about 2500-3500 ft/min. Tip  
speeds for continuous procedures most generally range  
between about 800 and about 3000 ft/min.

The dispersion process is typically carried  
15 out in a vessel which enables the powder-forming  
process to be conducted at elevated temperature and  
pressure. In the usual batch process, all of the  
ingredients are charged to the vessel and the mixture  
is heated to a temperature above the melt point of the  
20 copolymer. While the temperature will vary depending  
on the specific polymer being used, it will typically  
range from about 175°C to about 250°C. Since the  
fluidity of polymers is temperature related, it may be  
desirable to carry out the process at temperatures  
25 substantially above the melt point of the copolymer to  
facilitate formation of the dispersion; however, the  
temperature should not exceed the thermal degradation  
temperature of the polymer.

Stirring is commenced after the desired  
30 temperature is reached and continued until a  
dispersion of the desired droplet size is produced.

- 1 This will vary depending on the particular copolymer being used, temperature, amount and type of surfactant, and other process variables, but generally will range from about 5 minutes to about 2 hours.
- 5 Stirring is most commonly maintained for a period of from about 10 to about 30 minutes.

A polar liquid medium which is not a solvent for the copolymer is employed as the dispersant in the formation of the microfine powder support. These  
10 polar media are hydroxylic compounds and can include water, alcohols, polyols and mixtures thereof. The weight ratio of polar liquid medium to polymer ranges from about 0.8:1 to about 9:1 and, more preferably, from about 1:1 to about 5:1. It is particularly  
15 advantageous to use water as the dispersing medium or a liquid medium where water is the major component.

The pressure of the process is not critical so long as a liquid phase is maintained. In general, the pressure can range from about 1 up to about 250  
20 atmospheres. The process can be conducted at autogenous pressure or the pressure can be adjusted to exceed the vapor pressure of the liquid medium at the operating temperature. Most generally, with aqueous dispersions, the pressure will range from about 5 to  
25 about 120 atmospheres.

To form acceptable dispersions, one or more dispersing agents are necessarily employed. Useful dispersing agents are nonionic surfactants which are block copolymers of ethylene oxide and propylene  
30 oxide. Preferably, these nonionic surfactants are water-soluble block copolymers of ethylene oxide and

- 1 propylene oxide and have molecular weights greater  
than about 3500. Most will contain a major portion by  
weight of ethylene oxide and are obtained by  
polymerizing ethylene oxide onto preformed  
5 polyoxypropylene segments. The amount of nonionic  
surfactant employed can range from about 4 to about 50  
percent, based on the weight of the copolymer. Most  
preferably, the nonionic surfactant is present in a  
concentration of from about 7 to about 45 percent,  
10 based on the weight of the copolymer.

Useful nonionic surface active agents of the  
above type are manufactured and sold by BASF  
Corporation, Chemicals Division under the trademark  
Pluronic. These products are obtained by polymerizing  
15 ethylene oxide onto the ends of a preformed  
polyoxypropyllic base. Both the molecular weight of  
the polyoxypropylene base and the polyoxyethylene  
segments can be varied to yield a wide variety of  
products. One such compound found to be suitable in  
20 the practice of the process of this invention is the  
product designated as F-98 wherein a polyoxypropylene  
of average molecular weight of 2,700 is polymerized  
with ethylene oxide to give a product of molecular  
weight averaging about 13,500. This product contains  
25 20 weight percent propylene oxide and 80 weight  
percent ethylene oxide. Other effective Pluronic®  
surfactants include F-88 (M.W. 11,250, 20% propylene  
oxide, 80% ethylene oxide), F-108 (M.W. 16,250, 20%  
propylene oxide, 80% ethylene oxide), and P-85 (M.W.  
30 4,500, 50% propylene oxide, 50% ethylene oxide).  
These compounds, all containing at least about 50

1 weight percent ethylene oxide and having molecular  
weights of at least 4,500, are highly effective as  
dispersing agents for the aforementioned copolymers.

It is also possible to employ products sold  
5 under the trademark Tetronic which are prepared by  
building propylene oxide block copolymer chains onto  
an ethylenediamine nucleus and then polymerizing with  
ethylene oxide. Tetronic<sup>®</sup> 707 and Tetronic<sup>®</sup> 908 are  
most effective for the present purposes. Tetronic<sup>®</sup>  
10 707 has a 30 weight percent polyoxypropylene portion  
of 2,700 molecular weight polymerized with a 70 weight  
percent oxyethylene portion to give an overall  
molecular weight of 12,000. Tetronic<sup>®</sup> 908, on the  
other hand, has a 20 weight percent polyoxypropylene  
15 portion of 2,900 molecular weight polymerized with an  
80 weight percent oxyethylene portion to give an  
overall molecular weight of 27,000. In general,  
useful Tetronic<sup>®</sup> surfactants have molecular weights  
above 10,000 and contain a major portion by weight of  
20 ethylene oxide.

The powder-forming process may also be  
conducted in a continuous manner. If continuous  
operation is employed, the ingredients are  
continuously introduced to the system while removing  
25 the dispersion from another part of the system. The  
ingredients may be separately charged or may be  
combined for introduction to the autoclave.

The particulate copolymer supports and  
especially the microfine spheroidal powders described  
30 hereinabove are then used to prepare the supported  
metallocene catalysts of the instant invention.

1           In accordance with the present invention,  
the particulate copolymer is reacted with a metallated  
compound under conditions sufficient to form a  
metallated keto intermediate and an associate alcohol.

5           The metallated compounds employed in the  
present invention are well known to those skilled in  
the art and they include substituted or unsubstituted  
cyclopentadienylide, indenylide or fluorenylide  
compounds which contain a metal from Groups I-III of  
10 the Periodic Table of Elements. Illustrated examples  
of such compounds include, but are not limited to,  
sodium cyclopentadienylide, lithium  
cyclopentadienylide, potassium cyclopentadienylide,  
cyclopentadienylthallium, sodium pentamethyl  
15 cyclopentadienylide, lithium pentamethyl  
cyclopentadienylide, bis-(cyclopentadienyl) magnesium,  
bis-(cyclopentadienyl) calcium, sodium indenylide,  
lithium indenylide, sodium fluorenylide, lithium  
fluorenylide and the like. Of these metallated  
20 compounds, the cyclopentadienylide compounds are  
particularly preferred. Sodium cyclopentadienylide is  
the most preferred metallated compound employed in the  
present invention.

Typically in the present invention, from  
25 about 0.001 to about 10 mmol of metallized compound  
per gram of particulate copolymeric support is  
employed. This may mean that there is an excess  
amount of a metallated compound present relative to  
the amount of functional groups present on the  
30 copolymeric support. The maximum amount of metallated  
compound is determined by the number of functional

1 groups present on the copolymer support. More preferably, from about 0.01 to about 2 mmol metallated compound per gram of particulate support is employed in foregoing reaction step.

5 The above reaction of the particulate copolymer support and the metallated compound is carried out in an inert atmosphere, such as N<sub>2</sub> or Ar, and in the presence of an ether solvent such as tetrahydrofuran (THF), dimethyl ether, diethyl ether,  
10 di-n-propyl ether, diisopropyl ether, di-n-butyl ether, divinyl ether, diallyl ether, diphenyl ether, 1,4-dioxane, dimethoxyethane and the like. In a preferred embodiment of the present invention, the foregoing reaction is carried out in a N<sub>2</sub> atmosphere,  
15 and THF is used as the solvent. Solvents such as toluene, benzene and xylene are also contemplated in the present invention.

The aforementioned reaction of the particulate copolymer support and the metallated  
20 compound is conducted at a temperature of from about 0° to about 100°C for a period of time from about one hour to about five days. More preferably, the above reaction is conducted at a temperature of from about 15° to about 75°C for a period of time from about one  
25 day to about four days. Most preferably, the above reaction which results in the formation of the metallated keto- intermediate is conducted at a temperature of from about 20°C to about 30°C for up to about three days.

30 All or a portion of the solvent may be removed after this reaction and the intermediate

1 product produced may be washed, if desired. While it  
is not necessary, it is possible to wash and/or dry  
the intermediate product before contacting with the  
transition metal compound. Polymeric resins of high  
5 bulk density may be produced using catalysts which  
have been prepared without washing between contacting  
steps. If all or part of the solvent is removed from  
the intermediate product, it will be redispersed in  
fresh solvent prior to contacting with the transition  
10 metal compound.

The metallated keto intermediate is then  
contacted with a transition metal compound under  
conditions sufficient to bind the transition metal to  
the cyclopentadienyl, indenyl or fluorenyl ring which  
15 is bound through the keto-bridge to the particulate  
copolymer support material. This reaction provides  
the tethered metallocene solid catalyst composition of  
the instant invention.

Suitable transition metal compounds that are  
20 employed in the present invention are represent by  
general formula



wherein Cp is a substituted or unsubstituted  
cyclopentadienyl, indenyl or fluorenyl ring; M is a  
25 metal from Group IVB, VB or VIB of the Periodic Table  
of Elements; R'' is a hydride, a hydrocarbyl group  
having from about 1 to about 20 carbon atoms, an  
alkoxy group having from about 1 to about 12 carbon  
atoms, a substituted or unsubstituted aryl group  
30 containing from about 6 to about 12 carbon atoms, or  
NR''', wherein R''' is an alkyl containing from about 1



- 1 to about 12 carbon atoms; X is a halide; a is a 0 or  
1; b is 0-4; c is 0-4; and the sum of a, b and c is  
equal to the oxidation state of M.

Exemplary hydrocarbyl radicals are methyl,  
5 ethyl, propyl, butyl, acyl, isoamyl, hexyl, isobutyl,  
heptyl, octyl, nonyl, decyl, cetyl, 2-ethylhexyl,  
phenyl and the like.

Exemplary alkoxys are methoxy, ethoxy,  
propoxy, butoxy and the like. Of these, methoxy is  
10 most particularly preferred.

Exemplary halides include chloride, bromide,  
fluoride and iodide. Of these, chloride is most  
particularly preferred.

Suitable transition metal compounds that  
15 encompass the above formula include, but are not  
limited to, titanium trichloride, titanium  
tetrachloride, zirconium tetrachloride, hafnium  
tetrachloride, (cyclopentadienyl)titanium trichloride,  
(cyclopentadienyl)zirconium trichloride,  
20 (cyclopentadienyl)hafnium trichloride, zirconium  
tetramethyl, zirconium tetramethoxy, zirconium  
tetraethoxy, titanium tetramethyl, titanium  
tetramethoxy, titanium tetraethoxy,  
(cyclopentadienyl)zirconium tribromide,  
25 (cyclopentadienyl)zirconium trimethyl,  
(cyclopentadienyl)zirconium triphenyl,  
(cyclopentadienyl)zirconium trimethoxy, zirconium  
tetra((dimethyl)amide), zirconium  
tetra((diethyl)amide), cyclopentadienyl zirconium  
30 dimethylamide dichloride and the like.

1           Of these transition metal compounds,  
zirconium compounds are particularly preferred. The  
most preferred zirconium compounds are zirconium  
5 tetrachloride and cyclopentadienyl zirconium  
trichloride. It should be noted that the transition  
metal compounds may be associated with a suitable  
solvent. An example of such a compound is  $\text{ZrCl}_4(\text{THF})_2$   
where tetrahydrofuran is utilized as the solvent.

          The above reaction is carried out in the  
10 presence of a solvent mentioned hereinabove under an  
inert gas atmosphere. Moreover, the reaction is  
conducted at a temperature of from about 0°C to about  
100°C for a period of time up to about five days.  
More preferably, the reaction of the intermediate  
15 compound and the transition metal compound is carried  
out at a temperature of from about 15°C to about 75°C  
for a period of about 30 minutes to about two days.  
Most preferably, the reaction is conducted at a  
temperature of from about 20°C to about 30°C for a  
20 period of time up to about 24 hours.

          While it is not necessary, the supported  
metallocene catalyst of the present invention may be  
washed and dried after recovery. After the transition  
metal is reacted with the intermediate compound, the  
25 supported metallocene catalyst is recovered using  
conventional procedures, such as decantation and  
centrifugation, and is ready for use in  
polymerizations.

          Supported metallocene catalysts obtained in  
30 this manner are fine, free-flowing powders having  
particles not differing substantially in size, shape

1 and particle size distribution from that of the  
copolymer support material used for their preparation.  
The supported metallocene catalysts of the instant  
invention contain from about 0.01 up to about 10  
5 weight percent transition metal based on the total  
weight of said supported catalyst. More typically,  
transition metal contents will range from about 0.1 to  
about 2.0. The supported metallocene catalysts of  
this invention are generally employed with a  
10 cocatalyst, sometimes also referred to as a catalyst  
promoter or catalyst activator. The cocatalyst  
employed in the present invention contains at least  
one metal selected from Groups IA, IIA, IIB, IIIB, and  
IVB of the Periodic Table of Elements. Such  
15 cocatalysts are known and widely used in the  
polymerization art and can include metal alkyls, metal  
hydrides, metal alkylhydrides, and metal alkylhalides,  
such as alkyl lithium compounds, dialkylzinc compounds,  
trialkylboron compounds, trialkylaluminum compounds,  
20 alkylaluminum halides, alkylaluminum hydrides, and the  
like. Mixtures of cocatalytic agents can also be  
employed. Illustrative organometallic compounds which  
can be used as cocatalyst include n-butyllithium,  
diethylzinc, di-n-propylzinc, triethylboron,  
25 trimethylaluminum, triethylaluminum,  
triisobutylaluminum, tri-n-hexylaluminum,  
ethylaluminum dichloride, ethylaluminum dibromide,  
ethylaluminum dihydride, diethylaluminum chloride, di-  
n-propylaluminum chloride, and the like. Linear or  
30 cyclic aluminoxanes, which are preferred, such as  
those described in U. S. Patent Nos. 4,997,455 to

1 Wellborn, Jr. and 4,912,075 to Chang and dimeric  
compounds of the formula  $(Y)_2-Al-O-Al-(Y)_2$ , where each Y  
is the same or different and is an alkyl containing  
from about 1 to about 6, preferably from about 2 to  
5 about 4, carbon atoms can also be used as the  
cocatalyst. Preferred cocatalysts are the linear or  
cyclic aluminoxanes and the dimeric aluminum compounds  
described above. Methylaluminoxanes (MAO) are highly  
useful cocatalysts for the supported metallocene  
10 catalysts of the invention and is particularly  
preferred.

Cocatalysts are employed in amounts  
effective to promote (increase) the polymerization  
activity of the supported metallocene catalyst. The  
15 amount of cocatalyst used can vary widely but most  
generally the molar ratio of the metal of the  
cocatalyst, based on the transition metal compound,  
ranges from about 1:1 to about 10,000:1 and, more  
preferably, from about 50:1 to about 5,000:1. The  
20 catalyst may be activated in-situ by adding the  
cocatalyst and supported catalyst separately to the  
polymerization or the supported catalyst and activator  
may be pre-contacted before introduction to the  
polymerization reactor.

25 Cocatalysts for polymerization may be  
employed singly in the manner described, or in concert  
with other such modifiers, activators or promoters to  
enhance activity or influence resin properties. The  
use of cocatalyst modifiers is described, e.g. in U.S.  
30 Patent No. 5,334,567 to Menon et al. regarding  
halosilanes; U.S. Patent Nos. 4,559,318 to Smith et

- 1 al., 4,866,021 to Miro et al., 5,006,618 to Miro et  
al. regarding halocarbons; U.S. Patent No. 4,250,287  
to Matlack regarding aromatic esters; U.S. Patent Nos.  
3,786,032 to Jennings et al. and 4,611,038 to Brun et  
5 al. regarding additional organometallic activators,  
and U.S. Patent No. 5,275,991 to Buehler et al.  
regarding alkoxysilanes.

- Preferred compounds which may be employed as  
cocatalyst modifiers include halocarbons such as  
10 carbon tetrachloride, carbon tetrabromide,  
dichloromethane, dibromomethane, 1,1,1-trichloroethane  
and a number of commonly available chlorofluorocarbons  
(CFC's) and hydro-chlorofluorocarbons (HCFC's);  
halosilanes such as silicon tetrachloride,  
15 trichlorosilane, dichlorosilane; and alkoxysilanes  
such as dimethoxysilane, diethoxysilane,  
diisopropoxysilane, trimethoxysilane and  
tetramethoxysilane.

- A highly preferred class of cocatalyst  
20 modifiers that may be used in the present invention  
are the phenylborate salts. This class of cocatalyst  
modifier is well known to those skilled in this art.  
Suitable examples of such modifiers include, but are  
not limited to, triethylammonium tetraphenylborate,  
25 tri(n-butyl)ammonium tetraphenylborate,  
trimethylammonium tetraphenylborate,  
dimethyldiphenylammonium tetraphenylborate,  
methylpyridinium tetraphenylborate, benzylpyridinium  
tetraphenylborate, trimethylsulfonium  
30 tetraphenylborate, triethylammonium  
tetrakis(pentafluorophenyl) borate, triphenylammonium

- 1 tetrakis(pentafluorophenyl) borate,  
methyldiphenylammonium tetrakis(pentafluorophenyl)  
borate, anilinium tetrakis(pentafluorophenyl) borate,  
methylanilinium tetrakis(pentafluorophenyl) borate,  
5 dimethyl(m-nitroanilinium tetrakis(pentafluorophenyl)  
borate, pyridinium tetrakis(pentafluorophenyl) borate,  
N-methylpyridinium tetrakis(pentafluorophenyl) borate,  
trimethylsulfonium tetrakis(pentafluorophenyl) borate,  
tetraphenylphosphonium tetrakis(pentafluorophenyl)  
10 borate, triphenylphosphonium  
tetrakis(pentafluorophenyl) borate, hexafluoroarsenic  
acid triethylammonium and the like.

The catalyst of the invention can be used in  
virtually any polymerization procedure where supported  
15 metallocene catalysts have heretofore been utilized.  
This includes both gas phase (stirred or fluidized  
bed) polymerizations and solution polymerizations.  
They are highly effective for stirred bed and  
fluidized bed polymerization processes which are  
20 carried out in the substantial absence of a liquid  
reaction medium. Such procedures are well known and  
described in the prior art and may be conducted in a  
single reactor or in multiple reactors connected in  
series. The catalysts are equally effective for use  
25 in particle form (slurry) processes which are also  
described in the prior art. These polymerizations are  
carried out in a liquid organic medium in which the  
catalyst is suspended. A pressure sufficient to  
maintain the organic diluent and at least a portion of  
30 the monomer in the liquid phase is maintained.

1           The supported metallocene catalysts of the  
invention are useful for the preparation of  
homopolymers and copolymers of alpha-olefins  
containing from about 2 to about 8 carbon atoms. Most  
5   preferably, they are used to produce polymers  
comprised predominantly of ethylene and/or propylene  
with densities ranging from about 0.90 to about 0.97  
and having a desirable balance of rheological and  
physical properties making such polymers useful in  
10 applications such as blow molding, injection molding,  
rotomolding, rotolining, extrusion, coextrusion, film  
forming and the like.

          Moreover, the polymers produced herein have  
the same morphology as the supported catalyst used in  
15 the polymerization process. That is, the polymers  
produced by the instant process have substantially  
spherical particles and a median particle size which  
depends on both the median particle size of the  
catalyst particles and the amount of polymer produced  
20 per unit amount of catalyst employed in the  
polymerization. The median particle size can thus  
range from about 10 to about 5000 microns.  
Prepolymerization methods may be used to further  
improve upon the particle size of the polymer  
25 produced. Such prepolymerization methods are well  
known to those skilled in the art. Furthermore, the  
polymer particles produced in the present invention  
are compatible with the functionalized copolymeric  
supports. Thus, no residual gels are formed during  
30 the polymerization process which are attributable to  
the catalyst support.

1           The following examples are given to  
illustrate the scope of the invention. As will be  
apparent to those skilled in the art, numerous  
variations are possible and thus the scope of this  
5 invention should not be limited thereto.

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PREPARATION OF PARTICULATE SUPPORTS

An electrically heated two-liter Parr  
[trademark] pressure autoclave equipped with a  
5 thermowell and thermocouple connected to a digital  
display was used to prepare an ethylene-methyl  
acrylate copolymer (EMA) microfine powder support  
following the general procedure set forth in the U.S.  
Patent No. 3,422,049, the contents of which are  
10 incorporated herein by reference. The autoclave was  
equipped with an agitator and a Strahman [trademark]  
valve to permit rapid discharge of the hot polymer  
dispersion into a 5 gallon stainless steel discharge  
tank which was connected to the reactor via a 1"  
15 diameter stainless steel line. The hot dispersion was  
rapidly discharged into this tank containing  
approximately 6.5 liters of 20-23°C water at the  
completion of each run. The hot dispersion was  
introduced below the surface of the water. The  
20 autoclave agitator used had three, six-bladed,  
impellers and was driven by a 2 HP DC variable speed  
motor.

The powder produced in this operation was  
analyzed using laser light scattering to measure the  
25 size distribution thereof by volume. This technique  
used the principle of diffraction of the particles as  
the measurement means. A Model 2600C Malvern Particle  
Size Analyzer with proper lens configuration for the  
expected particle size interfaced with a computer was  
30 used. It read the diffraction pattern and digitally  
performed the necessary integrations. For the powder

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- 1 analysis, water was charged to the water bath and  
circulated through the sample measuring chamber.  
After obtaining the baseline measurement, the agitator  
and sonic vibrator were activated and the copolymer  
5 powder was added to the water bath until the  
obscuration reading was 0.3. Mixing and circulation  
were controlled to obtain acceptable dispersion  
without excessive foaming. A drop of liquid detergent  
was added to facilitate dispersion. After eight  
10 minutes agitation, measurements were commenced and the  
size distribution data was automatically tabulated.  
The cumulative volume undersize and volume frequency  
was tabulated for 32 size classes together with useful  
derived parameters. A logarithmic plot was also  
15 produced. Duplicate runs were made for each copolymer  
powder sample. The particle size reported in the  
examples was the median diameter  $D(v,0.5)$  for the  
volume distribution curve. The range reported in the  
examples was for 80 percent of the volume distribution  
20 curve, i.e., from  $D(v,0.1)$  to  $D(v,0.9)$ . In other  
words, ten percent of the powder particles were sized  
below the recited lower limit and 10 percent of the  
powder particles were larger than the upper recited  
particle size limit. This range provides a  
25 convenient means of comparing powders.

Following the procedure of Example I of U.  
S. Patent No. 3,422,049, a particulate microfine  
support was produced from an ethylene-methyl acrylate  
copolymer containing 16.5 wt.% methyl acrylate having  
30 a density of 0.939, a melt index of 6.0, a melting  
point, as determined by Differential Scanning

1 Colorimetry using the procedures of ASTM Test  
Procedures D-3417 and D-3418, of 86°C, and a VICAT  
Softening Point, as determined by ASTM Test Procedure  
D-155, Condition B, of 57°C.

5 In the above powder preparation, 450 grams  
of the copolymer was combined with 180 grams  
dispersing agent (Pluronic F-98) and 810 grams water.  
The reactor was sealed, heated and when the  
temperature reached about 210°C agitation (about 3200-  
10 3340 rpm)  
was commenced.

The powder thus prepared had a median  
particle size,  $D(v,0.5)$  of about 32.4 microns and a  
particle size range (in microns for 80% of the volume  
15 distribution curve) of about 14.3 - 61.6 microns.  
Furthermore, the EMA support prepared from the above  
procedure was a free-flowing powder comprised of  
discrete particles having spherical morphology, i.e.,  
the individual particles were spherical or  
20 substantially spherical in shape.

The EMA copolymer support used in the  
following examples was also more fully characterized  
and was found to have a surface area of about 2.1  
 $m^2/g$ , a pore volume of 0.021 cc/g and an average pore  
25 radius of 203 Å as determined by the Brunauer, Emmett,  
Teller (BET) method. These measurements were carried  
out using an AUTOSORB-6 [trademark] instrument and the  
physical measurements were determined using techniques  
described in S. Lowel et al., "Powder Surface Area and  
30 Porosity", 2nd Ed., Chapman and Hall, London, 1984.  
Furthermore, the copolymer support had a weight

- 1 average molecular weight ( $M_v$ ) of 110,400, number  
average molecular weight ( $M_n$ ) of 24,700 and MWD ( $M_v/M_n$ )  
of 4.50.

5 Additionally, a particulate support was  
obtained by cryogenically grinding EMA. Cryogenic  
grinding of this sample was conducted by mechanical  
means, using a Wiley mill which was equipped with a  
recirculating refrigerant. The polymer sample, i.e.  
EMA, was ground along with dry ice so as to not incur  
10 polymer melting. The polymer was also ground so as to  
pass through a 20 mesh screen size. The resulting  
ground powder has an average particle size of about  
590 microns and a particle size distribution of about  
297 to about 840 microns.

- 15 The microfine EMA copolymer support and the  
cryogenic ground support were employed in the  
preparation of the supported tethered metallocene  
catalysts in the examples which follow.

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1        PREPARATION OF SUPPORTED TETHERED METALLOCENE  
         CATALYSTS AND POLYMERIZATIONS

5    Example I:

         To illustrate the preparation of a supported  
metallocene catalyst of the instant invention, five  
(5.0) grams of the ground EMA support material  
prepared above was slurried with 75 ml dry THF under a  
10    nitrogen atmosphere in a 250 ml round-bottom Schlenk  
flask equipped with a stirring bar. One (1.0) ml of  
2.0M sodium cyclopentadienylide (NaCp) in THF (2.0  
mmol) was added via syringe to the slurry under N<sub>2</sub> at  
room temperature. The above reaction proceeded for  
15    about 72 hours, at which time a purple-red color was  
noted on the EMA support. Without wishing to be bound  
by any theory, this purple-red color is believed to be  
attributed to the electron-delocalized complex, i.e.  
the intermediate, formed upon bonding to the EMA.

20            To illustrate that a complex was formed on  
the EMA support, the intermediate was analyzed using a  
Nicole 60SXR FTIR. Upon spectral subtraction of the  
EMA support, a small peak at 1650 cm<sup>-1</sup> corresponding to  
a carbonyl stretch was identified. This stretch was  
25    in agreement with values reported in the literature  
for related keto-cyclopentadienides, and thus  
suggested that a unique carbonyl species, i.e. a keto-  
cyclopentadienide intermediate, had been formed on the  
polymer backbone.            The intermediate  
30    ("EMA/NaCp"), was isolated, washed free of excess NaCp

- 1 with heptane, and then dried in vacuo. The dried intermediate was then reslurried in fresh THF.

- A THF solution of  $\text{ZrCl}_4(\text{THF})_2$  (0.377g;  
5 0.999 mmol) was added via cannula at a target loading of about 0.2 mmol Zr/g EMA. The reaction proceeded for about two hours after which the product was filtered and washed with fresh THF (100 ml) to remove any unreacted  $\text{ZrCl}_4$  and possibly any unbound  $\text{Cp}_2\text{ZrCl}_2$ .  
10 The washed product was then dried in vacuo to give a metallocene catalyst supported through one or both of its cyclopentadienyl rings.

- Analysis of the metallocene catalyst revealed that the catalyst contained 0.56% Zr (0.06  
15 mmol Zr/g EMA).

- The catalyst was used to prepare ethylene homopolymers. The polymerization was conducted in a one liter autoclave reactor which was charged with 500 ml dried, deoxygenated isobutane. Hydrogen was added  
20 to control the molecular weight and a modified methylaluminoxane, obtained from Texas Alkyls as a 2.24M Al concentrated solution in heptane (MMAO-3A), was used as the cocatalyst. The details of the polymerization conditions as well as the  
25 characteristics of the resins produced are provided in Table 1.

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## 1 EXAMPLE II:

A supported metallocene catalyst containing the ground EMA support of Example I was prepared as follows:

5 4.06 grams of ground EMA was placed in a 250 ml roundbottom Schlenk flask equipped with a stirbar and was thereafter slurried with 50 ml of dry THF. One (1.00) ml of 2.0M NaCp in THF (2.0 mmol) was added via syringe to the slurried EMA while under nitrogen  
10 and at room temperature and the reaction was allowed to proceed with stirring for 72 hours. Over the course of the reaction time, the solution and ultimately the polymer took on a purple color. Once the reaction was completed, the THF was removed in  
15 vacuo to the point where the polymer was clumpy, but had excess THF. Approximately 200 ml of heptane was then added, the slurry was stirred briefly, then settled. A brackish brown supernatant was decanted off via cannula and discarded. The treated polymer  
20 was washed a second time with 200 ml heptane and decanted. A golden brown material remained which was dried in vacuo.

The remaining golden brown material was slurried once again in THF, then a solution of 0.105 g  
25 CpZrCl<sub>4</sub> (0.4 mmol) in 50 ml THF was added to the slurry. In the first 10 minutes, after addition, both the polymer and the solution changed to a wheaten yellow color. The reaction was concentrated down to approximately 25 ml THF and then was stirred overnight.  
30 at room temperature. The THF was filtered off, then the remaining catalyst was washed twice with 30 ml of

- 1 heptane and dried in vacuo to give a metallocene  
catalyst supported through a bridge to only one  
cyclopentadienyl ring. 2.7 Grams of a light caramel  
colored powder was recovered. Analysis revealed that  
5 the catalyst contained 0.53% Zr (0.058 mmolZr/g).

The catalyst was used to polymerize  
ethylene. The details of the polymerization in  
isobutane are provided in Table 1 whereas the  
polymerization data in toluene are tabulated in Table

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## 1 EXAMPLE III:

A supported metallocene catalyst containing the aforementioned particulate microfine EMA copolymer support was prepared and used for the polymerization of ethylene in this example. Specifically, the supported metallocene catalyst was prepared as follows:

5.2 grams of the particulate microfine EMA support, was placed in a 250 ml roundbottom Schlenk flask equipped with an egg-shaped stirbar and was slurried with 75 ml of dry THF. Two (2.00) ml of 2.0M NaCp in THF (4.0 mmol) was added via syringe to the slurried EMA, while under nitrogen and at room temperature, and the reaction was allowed to proceed with stirring for 4 days. Over the course of the reaction the solution and ultimately the polymer took on a caramel color. Once complete, the THF was filtered without prior reduction of volume. The polymer was washed once with heptane, filtered, then dried in vacuo to produce a grayish-purple powder.

The dried intermediate was again slurried in a 20 ml of THF, then a solution of 0.153 grams CpZrCl<sub>2</sub> (0.582 mmol) in 30 ml of THF was added to the slurry. Upon addition of the solution, the polymer reverted to a caramel color. The reaction was stirred overnight at room temperature, then was filtered. The powder was washed twice with heptane and dried in vacuo. 4.53 Grams of a light purple-grey powder was recovered.

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1           The resulting catalyst contained 0.44% Zr  
          (0.048 mmol Zr/g). The polymerization details are  
          tabulated in Table 1.

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## 1 EXAMPLE IV:

A supported metallocene catalyst containing the particulate microfine EMA support material was prepared as follows:

- 5 5.0 grams of particulate microfine EMA support was placed in a 250 ml roundbottom Schlenk flask equipped with stirbar and was slurried with 75 ml of dry THF. 4.50 ml of 2.0M NaCp in THF (9.0 mmol) was added via syringe to the slurried EMA while under  
10 nitrogen and at room temperature. The reaction was allowed to proceed with stirring for 4 days. Over the course of the reaction, the solution and ultimately the polymer took on a purple color. After the 4 days, THF was removed in vacuo. The polymer was washed with  
15 50 ml of fresh THF and filtered, leaving a grayish-purple powder.

- The dried intermediate was again slurried in 50 ml of THF, then a solution of 1.0 grams  $\text{ZrCl}_4(\text{thf})_2$  (2.65 mmol) in 50 ml of THF was added to the slurry.  
20 Upon addition of the solution, the polymer changed to a flaxen-yellow color. The reaction was stirred for one hour at room temperature, then the THF was filtered off, leaving a grayish polymer powder. The filtrate, which had a yellowish tint, was discarded.  
25 The powder was washed once with heptane, then filtered and dried in vacuo. 4.80 Grams of a light purple-grey powder were recovered.

The catalyst contained 0.72% Zr (0.079 mmol Zr/g).

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1            Table 1: Slurry Polymerization Results  
                                 with Isobutane

		I	I	II	III
5	Catalyst wt. (g)	0.33	0.34	0.15	0.36
	H <sub>2</sub> (mmol)	4	4	4	4
	Rx Temp. (°C)	90	70	70	90
	Rx Pressure (psig)	550	500	450	500
10	Al/Zr	2200	2100	6400	1300
	Time (min)	60	60	30	60
	Activity (g/g cat·hr)	479	360	1196	171
	MI <sup>1</sup>	1.26	0.32	0.239	1.11
15	MIR <sup>2</sup>	24.3	27.9	30.46	33.2
	MW <sup>3</sup>	70,700	110,200	105,200	190,790
	MWD <sup>4</sup>	2.4	2.7	3.0	5.6

20 Determined by ASTM D-1238, Condition E, reported  
as g/10 minutes.

<sup>2</sup> Determined by flotation in a density gradient column after annealing an extrudate sample for 30 minutes at 100°C to approach equilibrium crystallinity.

25 Weight average molecular weight determination was made using a Waters GPC on a mixed sized, crosslinked divinylbenzene column with 1,2,4-trichlorobenzene as a solvent at 135°C with a refractive index detector.

<sup>1</sup> The ratio of  $M_w$  vs  $M_n$ , i.e., MWD, was also determined by GPC.

1            Table 2: Slurry Polymerization Results  
    in Toluene

		II	II	II
5	Catalyst wt. (g)	0.18	0.17	0.16
	H <sub>2</sub> (mmol)	4	4	4
	Rx Temp. (°C)	70	70	90
10	Rx Pressure (psig)	200	400	200
	Al/Zr	5333	2259	2400
	Time (min)	60	60	60
	Activity (g/g cat·hr)	1092	653	679
15	MI <sup>1</sup>	1.91	0.73	23.86
	MIR <sup>2</sup>	18.9	17.8	NA
	MW <sup>1</sup>	85,800	128,800	50,600
	MWD <sup>1</sup>	2.4	2.3	1.8

20        1     Determined by ASTM D-1238, Condition E, reported as g/10 minutes.

          2     Determined by flotation in a density gradient column after annealing an extrudate sample for 30 minutes at 100°C to approach equilibrium crystallinity.

25        1     Weight average molecular weight determination was made using a Waters GPC on a mixed sized, crosslinked divinylbenzene column with 1,2,4-trichlorobenzene as a solvent at 135°C with a refractive index detector.

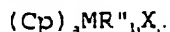
          1     The ratio of Mw vs Mn, i.e., MWD, was also  
 30        determined by GPC.

1 What is claimed is:

1. A supported metallocene catalyst useful  
for polymerizing olefins comprising the product which  
5 is prepared by the steps of:

(a) reacting a particulate olefin copolymer  
support which comprises discrete particles having a  
median particle size ranging from about 1 up to about  
1500 microns, a pore volume of less than 0.1 cc/g and  
10 a surface area of less than about 15 m<sup>2</sup>/g, wherein  
said olefin copolymer has a melt index of from about  
0.1 to about 400 and containing from about 50.1 to  
about 99.9 weight percent C<sub>2</sub>,  $\alpha$ -olefin and from about  
0.1 to about 49.9 weight percent of an acrylate, with  
15 a metallated compound containing a metal from Groups  
I-III of the Periodic Table of Elements under  
conditions sufficient to form a metallated keto-  
intermediate;

(b) contacting said metallated keto-  
20 intermediate of step (a) with a transition metal  
compound having the formula



wherein Cp is a substituted or unsubstituted  
cyclopentadienyl, indenyl or fluorenyl ring; M is a  
25 metal from Group IVB, VB and VIB of the Periodic Table  
of Elements; R'' is a hydride, a hydrocarbyl group  
having from about 1 to about 20 carbon atoms, an  
alkoxy group having from about 1 to about 12 carbon  
atoms, a substituted or unsubstituted aryl group  
30 containing from about 6 to about 12 carbon atoms, or  
NR'', wherein R'' is an alkyl containing from about 1

- 1 to about 12 carbon atoms; X is a halide; a is 0 or 1;  
b is 0-4; c is 0-4; and the sum of a, b, and c is  
equal to the oxidation state of M; and  
(c) recovering said contact product of step  
5 (b).

2. The supported metallocene catalyst of  
Claim 1 wherein said acrylate has the formula:



10 wherein R is hydrogen or methyl and R' is an alkyl  
group having from about 1 to about 12 carbon atoms or  
an aryl group having from about 6 to about 12 carbon  
atoms.

15 3. The supported metallocene catalyst of  
Claim 2 wherein R is hydrogen and R' is a C<sub>1-12</sub> alkyl  
group.

4. The supported metallocene catalyst of  
Claim 3 wherein said acrylate is methyl acrylate.

20 5. The supported metallocene catalyst of  
any one of Claims 1-4 wherein said particles range in  
size from about 1 to about 1000 microns and the olefin  
copolymer contains from about 70 to about 99 weight  
percent C<sub>2</sub>, α-olefin and from about 1 to about 30  
25 weight percent of said acrylate.

6. The supported metallocene catalyst of  
Claim 5 wherein said olefin copolymer contains from  
about 80 to about 95 weight percent ethylene and from  
about 5 to about 20 weight percent of said acrylate.

30 7. The supported metallocene catalyst of  
any one of Claims 1-6 wherein said olefin copolymer is

1 selected from the group consisting of a copolymer of  
ethylene-methyl acrylate, a copolymer of ethylene-  
ethyl acrylate and a copolymer of ethylene-n-butyl  
acrylate.

5           8. The supported metallocene catalyst of  
Claim 7 wherein said olefin copolymer is ethylene-  
methyl acrylate.

10           9. The supported metallocene catalyst of  
any one of Claims 1-8 wherein said support is a  
microfine powder comprised of particles which are  
spherical or substantially spherical in shape and has  
a median particle size ranging from about 1 to about  
500 microns, from about 5 to about 300 microns, or  
from about 20 to about 200 microns.

15           10. The supported metallocene catalyst of  
any one of Claims 1-9 wherein said metallated compound  
is a substituted or unsubstituted cyclopentadienylide,  
indenylide or fluorenylide compound.

20           11. The supported metallocene catalyst of  
Claim 10 wherein said metallated compound is a  
compound selected from the group consisting of sodium  
cyclopentadienylide, lithium cyclopentadienylide,  
potassium cyclopentadienylide, lithium  
pentamethylcyclopentadienylide, bis-(cyclopentadienyl)  
25 magnesium, bis-(cyclopentadienyl) calcium,  
cyclopentadienylthallium, sodium  
pentamethylcyclopentadienylide, sodium indenylide,  
lithium indenylide, sodium fluorenylide and lithium  
fluorenylide.

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1           12. The supported metallocene catalyst of  
any one of Claims 1-11 wherein from about 0.001 to  
about 10 mmol metallated compound per gram particulate  
olefin copolymer support is employed in step (a).

5           13. The supported metallocene catalyst of  
any one of Claims 1-12 wherein steps (a) and (b) are  
carried out in an inert atmosphere in the presence of  
an ether solvent or an aromatic solvent.

10           14. The supported metallocene catalyst of  
Claim 13 wherein said inert atmosphere is a N<sub>2</sub> or an  
Ar gas atmosphere.

15           15. The supported metallocene catalyst of  
Claim 13 wherein said ether solvent is selected from  
the group consisting of tetrahydrofuran, dimethyl  
ether, diethyl ether, di-n-propyl ether, diisopropyl  
ether, di-n-butyl ether, divinyl ether, diallyl ether,  
diphenyl ether, dimethoxyethane and 1,4 dioxane.

20           16. The supported metallocene catalyst of  
any one of Claims 1-15 wherein step (a) is conducted  
at a temperature of from about 0°C to about 100°C for  
a period of time of about 1 hr to about 5 days.

25           17. The supported metallocene catalyst of  
any one of Claims 1-16 wherein said intermediate of  
step (a) may optionally be washed and dried prior to  
performing step (b).

30           18. The supported metallocene catalyst of  
any one of Claims 1-12 wherein said transition metal  
compound is selected from the group consisting of  
titanium trichloride, titanium tetrachloride,  
zirconium tetrachloride, hafnium tetrachloride,  
(cyclopentadienyl)titanium trichloride,

- 1 (cyclopentadienyl)zirconium trichloride,  
(cyclopentadienyl)hafnium trichloride, zirconium  
tetramethyl, zirconium tetramethoxy, zirconium  
tetraethoxy, titanium tetramethyl, titanium  
5 tetramethoxy, titanium tetraethoxy,  
(cyclopentadienyl)zirconium tribromide,  
(cyclopentadienyl)zirconium trimethyl,  
(cyclopentadienyl)zirconium triphenyl, zirconium  
tetra((dimethyl)amide), zirconium  
10 tetra((diethyl)amide), cyclopentadienyl zirconium  
dimethylamide dichloride and  
(cyclopentadienyl)zirconium trimethoxy.

19. The supported metallocene catalyst of  
any one of Claims 1-18 wherein step (b) is conducted at  
15 a temperature of from about 0°C to about 100°C for a  
period of time up to about 5 days.

20. The supported metallocene catalyst of  
any one of Claims 1-19 wherein said supported  
metallocene contains from about 0.01 up to about 10  
20 weight percent of said transition metal, based on the  
total weight of said catalyst.

21. An alpha-olefin polymerization catalyst  
system comprising the supported metallocene catalyst  
obtained in any one of Claims 1-20 and at least one  
25 cocatalyst compound containing a metal from Groups IA,  
IIA, IIB, IIIB or IVB of the Periodic Table of  
Elements.

22. The alpha-olefin polymerization  
catalyst system of Claim 21 wherein said cocatalyst is  
30 a metal alkyl, metal hydride, metal alkylhydride or  
metal alkylhalide.

- 1           23. The alpha-olefin polymerization  
catalyst system of Claim 22 wherein the cocatalyst is  
a cyclic or linear aluminoxane.
- 5           24. The alpha-olefin polymerization  
catalyst system of Claim 23 wherein the cocatalyst is  
methylaluminoxane.
- 10          25. The alpha-olefin polymerization  
catalyst system of any one of Claims 21-24 wherein the  
cocatalyst is added in a molar ratio of about 1:1 to  
about 10,000:1 based on the transition metal compound  
of said catalyst.
- 15          26. The alpha-olefin polymerization  
catalyst system of any one of Claims 21-25 further  
comprising a cocatalyst modifier.
- 20          27. The alpha-olefin polymerization  
catalyst system of Claim 26 wherein the cocatalyst  
modifier is a halosilane, a halocarbon, an aromatic  
ester, an organometallic compound, an alkoxysilane or  
a phenylborate salt.
- 25          28. The alpha-olefin polymerization  
catalyst system of Claim 27 wherein the phenyl borate  
salt is triethylammonium tetrphenylborate, tri(n-  
butyl)ammonium tetrphenylborate, trimethylammonium  
tetrphenylborate, dimethyldiphenylammonium  
tetrphenylborate, methylpyridinium tetrphenylborate,  
benzylpyridinium tetrphenylborate, trimethylsulfonium  
tetrphenylborate, triethylammonium  
tetrakis(pentafluorophenyl) borate, triphenylammonium  
tetrakis(pentafluorophenyl) borate,  
30   methyldiphenylammonium tetrakis(pentafluorophenyl)  
borate, anilinium tetrakis(pentafluorophenyl) borate,

1 methylanilinium tetrakis(pentafluorophenyl) borate,  
dimethyl(m-nitroanilinium tetrakis(pentafluorophenyl)  
borate, pyridinium tetrakis(pentafluorophenyl) borate,  
N-methylpyridinium tetrakis(pentafluorophenyl) borate,  
5 trimethylsulfonium tetrakis(pentafluorophenyl) borate,  
tetraphenylphosphonium tetrakis(pentafluorophenyl)  
borate, triphenylphosphonium  
tetrakis(pentafluorophenyl) borate and  
hexafluoroarsenic acid triethylammonium.

10 29. A process for (co)-polymerizing  $\alpha$ -  
olefins comprising polymerizing at least one C<sub>2</sub>-C<sub>4</sub>  $\alpha$ -  
olefin under polymerization conditions in the presence  
of the polymerization catalyst system of any one of  
Claims 21-28, wherein the cocatalyst is added in a  
15 molar ratio of about 1:1 to  
about 10,000:1 based on the transition metal compound  
of said catalyst.

20 30. The process of Claim 29, wherein said  
 $\alpha$ -olefin is (co)polymerized into a polymer or  
copolymer having substantially spherical particles  
whose median particle sizes range from about 10 to  
about 5000 microns.

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## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US96/06447

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C08F 4/02, 4/60

US CL : 502/109, 127

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 502/109, 127

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A,P	US 5,492,985 A (PEIFER ET AL) 20 February 1996.	1-6
Y	US 3,422,049 A (MCCLAIN) 14 January 1969, entire document.	1-6
Y	EP 0,522,581 A1 (IDEMITSU KOSAN COMPANY LIMITED) 13 January 1993, entire document.	1-6
Y	JP 6-56928 A (UBE INDUSTRIES, LTD.) 01 March 1994, see translation page 12.	1-6

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* "A"	Special categories of cited documents: document defining the general state of the art which is not considered to be of particular relevance	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E"	earlier document published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means	"Z"	document member of the same patent family
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

12 JUNE 1996

Date of mailing of the international search report

11 JUL 1996

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# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US96/06447

## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 7-30  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.  
☐ No protest accompanied the payment of additional search fees.